SALICYLIC ACID

The chief derivative of salicylic acid (melting point: 159°C, boiling point: 211°C, density: 1.565), which is used as a drug, is the methyl acetyl ester, known as *aspirin*.

The manufacture of salicylic acid follows carboxylation of sodium phenolate (Fig. 1). The sodium phenolate must be finely divided and exposed to the action of the carbon dioxide under pressure and heat in a heated ball

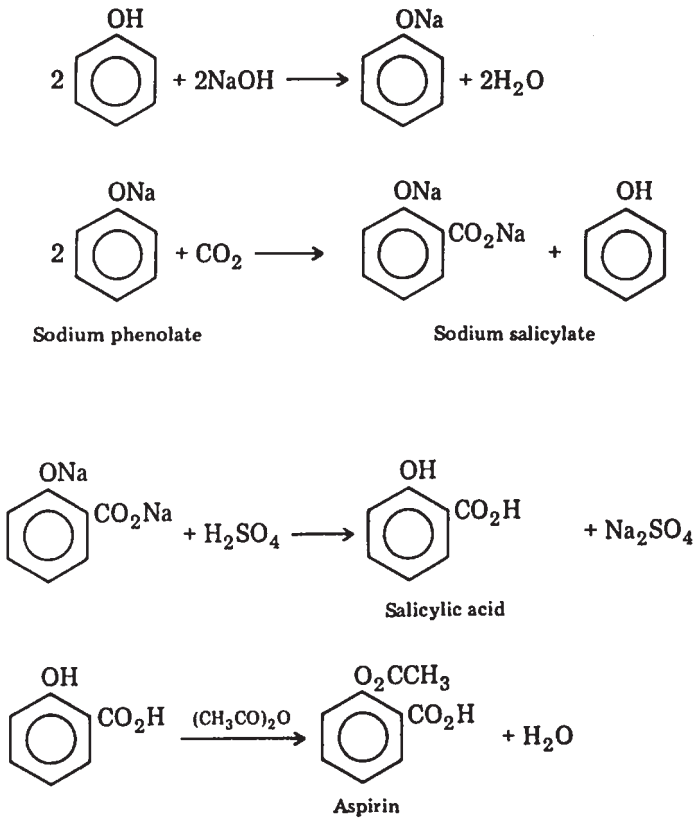


FIGURE 1 Chemistry of salicylic acid and aspirin production.

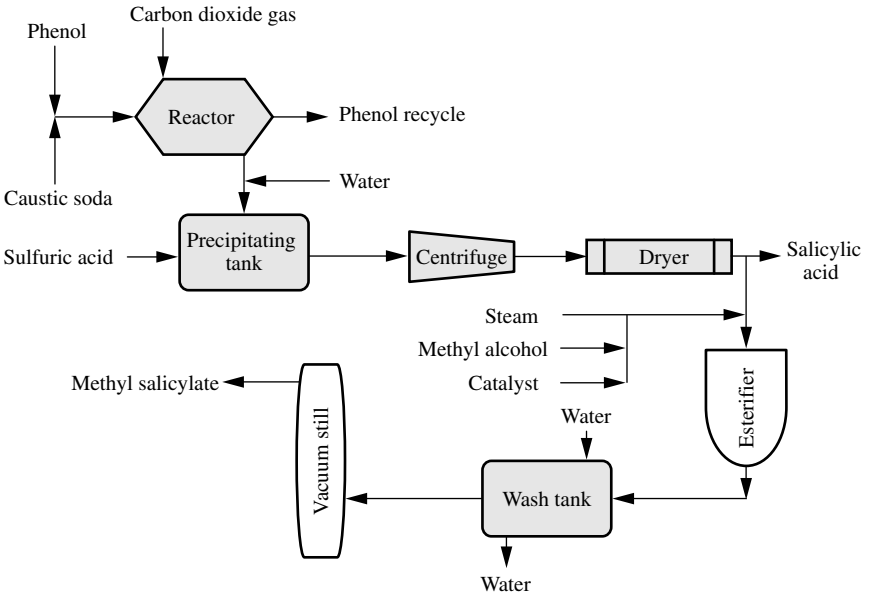


FIGURE 2 Manufacture of salicylic acid and aspirin.

mill reactor (Fig. 2). In the reactor at 130°C and vacuum, the sodium phenolate is reduced to a very dry powder, after which the carbon dioxide is introduced under pressure (700 kPa) and temperature (100°C) to form, first, sodium phenyl carbonate, which isomerizes to sodium salicylate. This can be dissolved out of the mill, and the salicylic acid decolorized by activated carbon and precipitated by addition of sulfuric acid, after which the salicylic acid is purified by sublimation.

To form aspirin, the salicylic acid is refluxed with acetic anhydride in toluene at 88 to 92°C for 20 hours. The reaction mixture is then cooled in aluminum cooling tanks, and the acetylsalicylic acid precipitates as large crystals that are separated by filtration or by centrifugation, washed, and dried.

See ***Aspirin.***

SILICA GEL

See ***Sodium Silicate.***

SILVER SULFITE

See ***Sulfurous Acid.***

SOAP

Soaps are the sodium or potassium salts of certain fatty acids obtained from the hydrolysis of triglycerides.

$$\text{Fat} + \text{NaOH} \rightarrow \text{glycerol} + \text{R–CO}_2^-\text{Na}^+$$

Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, palmitic, lauric, and myristic acids.

Manufacturing processes are both batch (in which the triglyceride is steam-hydrolyzed to the fatty acid without strong caustic, and then in a separate step it is converted into the sodium salt) or continuous.

The manufacture of soap (Fig. 1) involves continuous splitting (hydrolysis) and, after separation of the glycerin, neutralization of the fatty acids to soap. The procedure is to split, or hydrolyze, the fat, and then, after separation from the glycerol (glycerin) to neutralize the fatty acids with a caustic soda solution:

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \rightarrow 3C_{17}H35COOH + C_3H_5(OH)_5$$
$$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COONa + H_2O$$

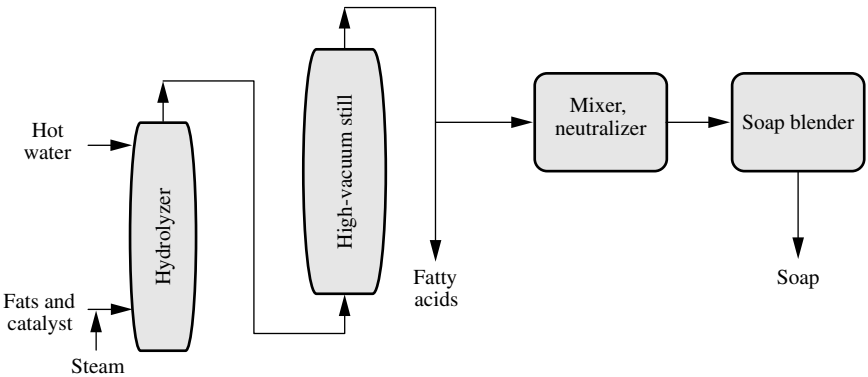


FIGURE 1 Manufacture of fatty acids and soap.

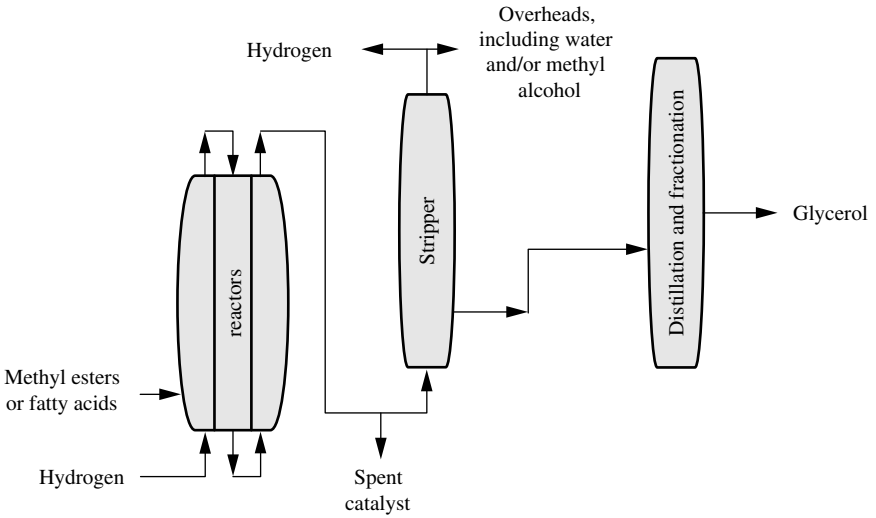


FIGURE 2 Hydrogenolysis of methyl esters to obtain fatty acids and glycerol (glycerin).

In continuous, countercurrent splitting, the fatty oil is deaerated under a vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower through a sparge ring (Fig. 2). The oil in the bottom contacting section rises because of its lower density and extracts the small amount of fatty material dissolved in the aqueous glycerol (glycerin) phase. At the same time, deaerated, demineralized water is fed to the top contacting section, where it extracts the glycerol dissolved in the fatty phase. After leaving the contacting sections, the two streams enter the reaction zone where they are brought to reaction temperature by the direct injection of high-pressure steam, and then the final phases of splitting occur. The fatty acids are discharged from the top of the splitter or hydrolyzer to a decanter, where the entrained water is separated or flashed off. The glycerol-water solution is then discharged from the bottom of an automatic interface controller to a settling tank.

SODIUM

Sodium is a silvery-white reactive metal that reacts violently with water and is usually preserved in containers under a nitrogen blanket or under dry, liquid kerosene.

The most important method of preparation of sodium is by the electrolysis of fused sodium chloride.

$$2NaCl \rightarrow 2Na + Cl_2$$

The cell for this electrolysis consists of a closed, rectangular, refractory-lined steel box with a carbon anode and an iron cathode. The anode and cathode are arranged in separate compartments to facilitate the recovery of the sodium and the chlorine. Sodium chloride has a high melting point (804°C), but calcium chloride is added to lower it, and the cell is operated at 600°C. The electrolyte is a eutectic of 33.3% sodium chloride arid 66.7% calcium chloride.

A sodium-calcium mixture collects at the cathode, but the solubility of calcium in sodium decreases with decreasing temperatures so that the heavier calcium crystals, which form as the mixture is cooled, settle back into the bath. The crude sodium is filtered at 105 to 110°C, giving sodium of 99.9% purity that is run molten into a nitrogen-filled tank car and allowed to solidify.

SODIUM BICARBONATE

Sodium bicarbonate (also called bicarbonate of soda or baking soda and mined as the ore nahcolite) can be made by treating soda ash with carbon dioxide and water at about 40°C in a contacting tower.

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

The suspension of bicarbonate formed is removed from the bottom of the tower, filtered, and washed on a rotary drum filter. The cake is then centrifuged and dried on a continuous belt conveyor at 70°C. Bicarbonate made in this fashion is about 99.9% pure.

Sodium bicarbonate is widely used in the food industry, in making rubber; in pharmaceuticals; as an antacid; in fire extinguishers, soap and detergents, rug cleaners, animal feeds, and textiles; in leather preparation; in soap, detergent, and paper manufacturing; for flue-gas scrubbing; and for many other diversified small-scale uses.

SODIUM BISULFITE

See ***Sulfurous Acid.***

SODIUM CARBONATE

Sodium carbonate (soda ash) was manufactured by the LeBlanc process (discovered in 1773) for many years in Europe. In this process, salt cake (sodium sulfate) reacts with limestone to give sodium carbonate and a side product, gypsum (calcium sulfate).

$$Na_2SO_4 + CaCO_3 \rightarrow Na_2CO_3 + CaSO_4$$

In 1864, Ernest Solvay, a Belgian chemist, invented his ammonia-soda process (Fig. 1), which has replaced the LeBlanc process.

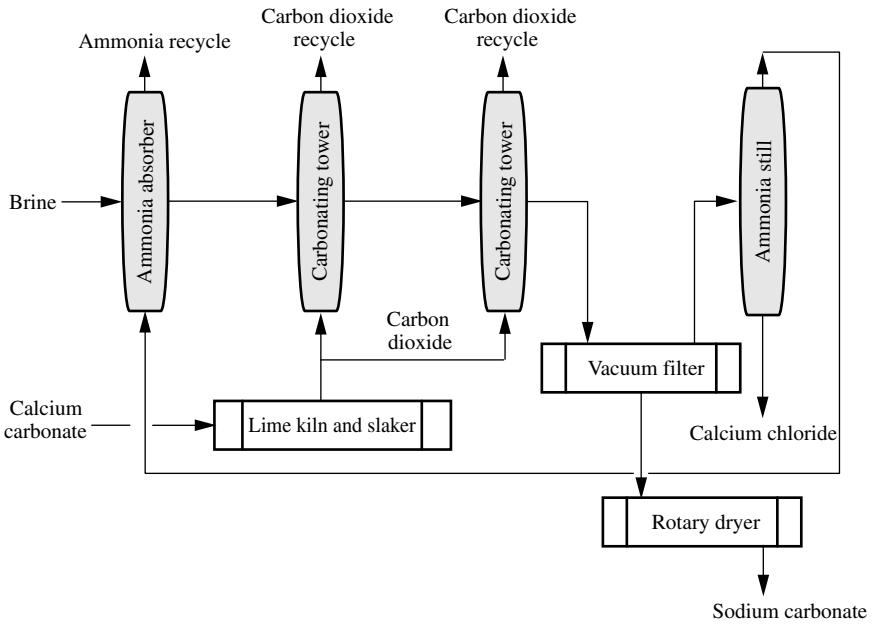


FIGURE 1 Manufacture of sodium carbonate (soda ash).

$$2NH_4OH + 2CO_2 \rightarrow 2NH_4HCO_3$$

$$2NH_4HCO_3 + 2NaCl \rightarrow 2NaHCO_3 + 2NH_4Cl$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

or

$$CaCO_3 + 2NaC1 \rightarrow Na_2CO_3 + CaCl_2$$

In the process (Fig. 1), the brine (salt solution) is mixed with ammonia in a large ammonia absorber. A lime kiln serves as the source of carbon dioxide, which is mixed with the salt and ammonia in carbonation towers to form ammonium bicarbonate and finally sodium bicarbonate and ammonium chloride. Filtration separates the less soluble sodium bicarbonate from the ammonium chloride in solution. The sodium bicarbonate is heated to 175°C in rotary dryers to give light soda ash and the carbon dioxide is recycled. Light soda ash is less dense than the natural material because holes are left in the crystals of sodium bicarbonate as the carbon dioxide is liberated. Dense soda ash, used by the glass industry, is manufactured from light ash by adding water and drying. The ammonium chloride solution goes to an ammonia still where the ammonia is recovered and recycled. The remaining calcium chloride solution is an important by-product of this process, although in large amounts it is difficult to sell and causes a disposal problem.

Natural trona ore is mostly $2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (45% Na_2CO_3, 36% $NaHCO_3$, 15% water + impurities). Processing this ore gives soda ash (Fig. 2) and solution mining method is in practice wherever possible.

Glass is the biggest industry using soda ash and consists of bottles and containers, flat glass, and fiberglass. In many other uses, soda ash competes directly with caustic soda as an alkali. The chemical of choice is then dependent on price and availability of the two.

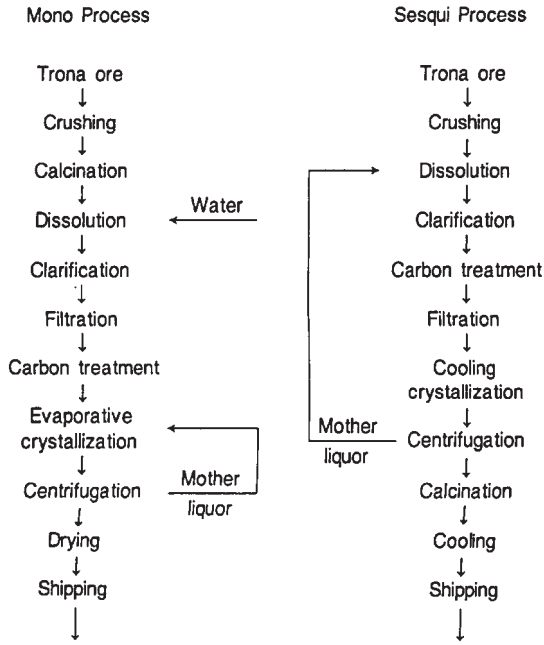


FIGURE 2 Manufacture of sodium carbonate from trona.

SODIUM CHLORATE

Sodium chlorate ($NaClO_3$) is manufactured by the electrolysis of saturated, acidulated brine mixed with sodium dichromate to reduce the corrosive action of the hypochlorous acid present (Fig. 1).

The brine solution is made from soft water or condensate from the evaporator and rock salt purified of calcium and magnesium. The rectangular steel cell is filled with either the brine solution or a recovered salt solution, made from recovered salt-containing chlorate, dissolved in condensate from the evaporator. Electrodes are graphite and steel for small cells, graphite and graphite for larger cells. The temperature of the cell is maintained at 40°C by cooling water.

The electrolysis step produces sodium hydroxide (NaOH) at the cathode and chlorine (Cl_2) at the anode, and mixing occurs with the formation of sodium hypochlorite (NaOCl) that is oxidized to chlorate.

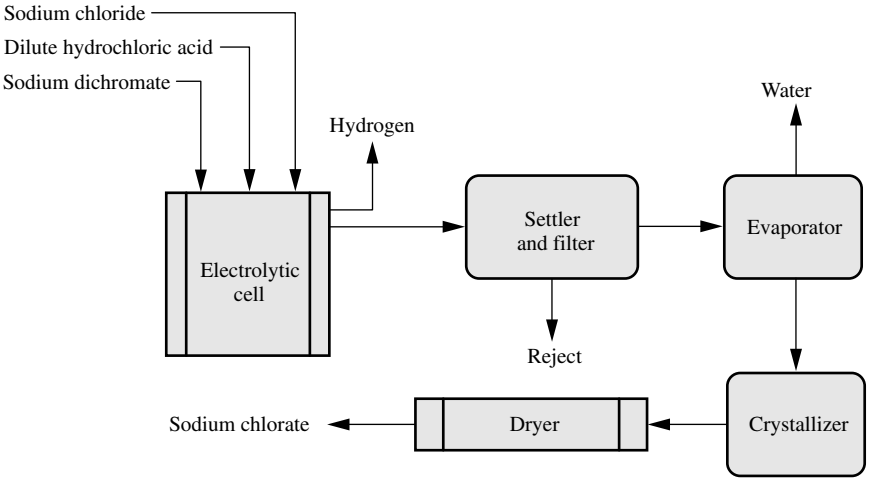


FIGURE 1 Manufacture of sodium chlorate.

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + C1_2$$

$$C1_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

The cell liquor is pumped to tanks where it is heated with steam to 90°C to destroy any hypochlorite present and the required amount of barium chloride is introduced to precipitate any chromate present.

The graphite mud from the electrodes and the barium chromate settle to the bottom of the tank and the clear liquor is pumped through a filter to the evaporator storage tanks. The liquor in the storage tank is neutralized with soda ash and evaporated, after which the liquor is allowed to settle to remove the sodium chloride. The settled liquid is filtered and cooled and the crystals of sodium chlorate that drop out are separated and dried.

Potassium chloride can be electrolyzed for the direct production of potassium chlorate, but, because sodium chlorate is so much more soluble, the production of the sodium salt is generally preferred. Potassium chlorate may be obtained from the sodium chlorate by a metathesis reaction with potassium chloride.

SODIUM CHLORIDE

Sodium chloride (salt, common salt, rock salt, and grainer salt) is a naturally occurring mineral.

There are three methods of salt production and purification: brine solution, rock salt mining, and the open pan or grainer process.

To produce sodium chloride from *brine*, water is pumped into the salt deposit and the saturated salt solution containing 26% salt, 73.5% water, and 0.5% impurities, is removed. Hydrogen sulfide is removed by aeration and oxidation with chlorine. Calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{3+}) are precipitated as the carbonates using soda ash and are removed in a settling tank. The brine solution can be sold directly or it can be evaporated to give salt of 99.8% purity.

Rock salt is produced from deep *mines* so that the salt is taken directly from the deposit. Salt obtained by this method is 98.5 to 99.4% pure.

In the *open pan* or *grainer salt* method, hot brine solution is held in an open pan approximately 4 to 6 meters wide, 45 to 60 meters long, and 60 cm deep at 96ºC. Flat, pure sodium chloride crystals form on the surface and fall to the bottom and are raked to a centrifuge, separated from the brine, and dried. A purity of 99.98% is obtained. A *vacuum pan* system (Fig. 1) is also available.

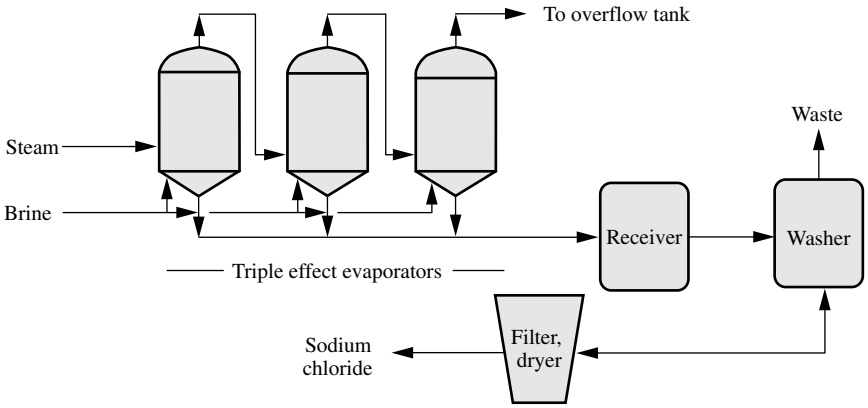


FIGURE 1 Vacuum pan system for producing sodium chloride.

SODIUM CHLORITE

Sodium chlorite ($NaClO_2$) is manufactured from chlorine dioxide, sodium hydroxide, and calcium hydroxide.

$$4NaOH + Ca(OH)_2 + C + 4ClO_2 \rightarrow 4NaClO_2 + CaCO_3 + 3H_2O$$

After filtering oil, the calcium carbonate, the solution of sodium chlorite ($NaClO_2$) is evaporated and drum-dried.

Sodium chlorite is a powerful and stable oxidizing agent and is capable of bleaching much of the coloration in cellulosic materials without weakening the cellulose fibers. It finds uses in the pulp and textile industries, particularly in the final whitening of kraft paper.

Besides being employed as an oxidizer, sodium chlorite is also the source of another chlorine compound, chlorine dioxide.

$$2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$$

Chlorine dioxide has 2½ times the bleaching power of chlorine and is important in water purification, for odor control, and for pulp bleaching.

SODIUM DICHROMATE

Sodium dichromate is manufactured from chromite, a chromium iron oxide containing approximately 50% chromic oxide (Cr_2O_3) with iron oxide (FeO), alumina ($A1_2O_3$), silica (SiO_2), and magnesium oxide (MgO).

In the process (Fig. 1), the ore is ground and mixed with ground limestone and soda ash, and roasted at approximately 1200°C in an oxidizing atmosphere. The sintered mass is crushed and leached with hot water to separate the soluble sodium chromate. The solution is treated with sulfuric acid to convert the sodium chromate to sodium dichromate plus sodium sulfate. Some of the sodium sulfate crystallizes in the anhydrous state from the hot solution during acidification as well as in the evaporators during concentration of the dichromate solution. From the evaporator, the hot, sat-

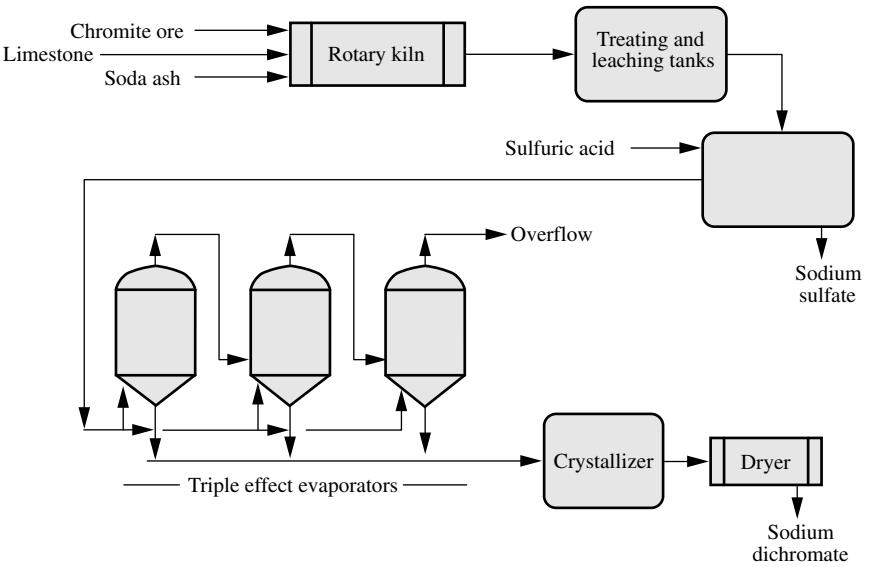


FIGURE 1 Manufacture of sodium dichromate.

urated dichromate solution is fed to the crystallizer, and then to the centrifuge and dryer.

Sodium dichromate is used as the starting material for producing the solutions of chromium salts employed in chrome leather tanning and in chrome mordant dyeing of wool cloth. Pigments, such as yellow lead chromate, are manufactured from sodium dichromate, as are also green chromium oxides for ceramic pigments. Other uses of sodium dichromate include the manufacture of chromium alloys and chromium plating of metals.

SODIUM HYDROXIDE

Sodium hydroxide (caustic soda, caustic) was made for many years by the *lime causticization* method, which involves reaction of slaked lime and soda ash.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

In 1892, the electrolysis of brine was discovered as a method for making both sodium hydroxide and chlorine, and since the 1960s it has been the only method of manufacture of sodium hydroxide (Fig. 1).

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + C1_2$$

The brine that is used for the electrolysis must be purified, and calcium, magnesium, and sulfate ions are removed by precipitation reactions.

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$$

$$2NaOH + MgCl_2 \rightarrow Mg(OH)_2 + 2NaCl$$

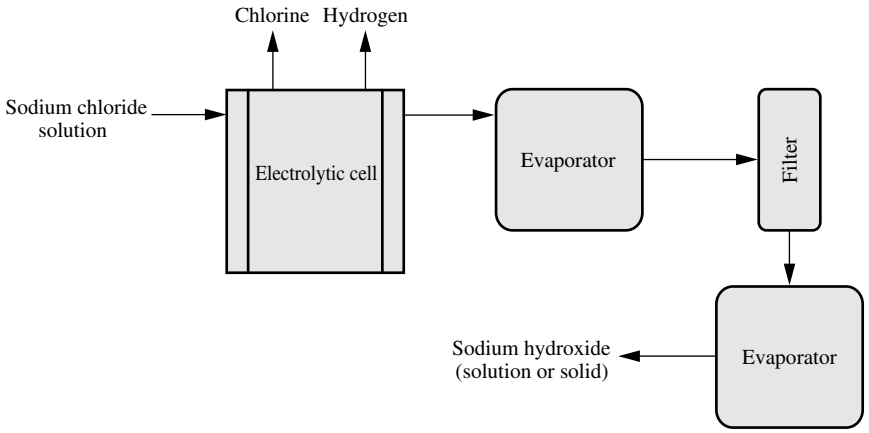


FIGURE 1 Manufacture of sodium hydroxide by the electrolysis of brine.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$$

Two types of cells are employed for the production of sodium hydroxide by electrolysis: the diaphragm cell (Fig. 2) the mercury cell (Fig. 3).

The diaphragm in the diaphragm cell (Fig. 2) prevents the diffusion of sodium hydroxide toward the anode. The anode solution level is maintained higher than in the cathode compartment to retard hack migration. If sodium hydroxide built up near the anode it would react with chlorine to give sodium hypochlorite as a side product.

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

Each cell is upward of 6 ft square and may contain 100 anodes and cathodes and a sodium hydroxide plant would have several circuits with approximately 90 cells in each circuit.

The mercury cell (Fig. 3) has no diaphragm but is made of two separate compartments. In the electrolyzing chamber the dimensionally stable anodes of ruthenium-titanium cause chloride ion oxidation that is identical to that of a diaphragm cell. The cathode is made of a sodium amalgam flowing across the steel bottom of the cell at a slight angle from the horizontal and promotes the reduction of sodium ions to the metal. The sodium

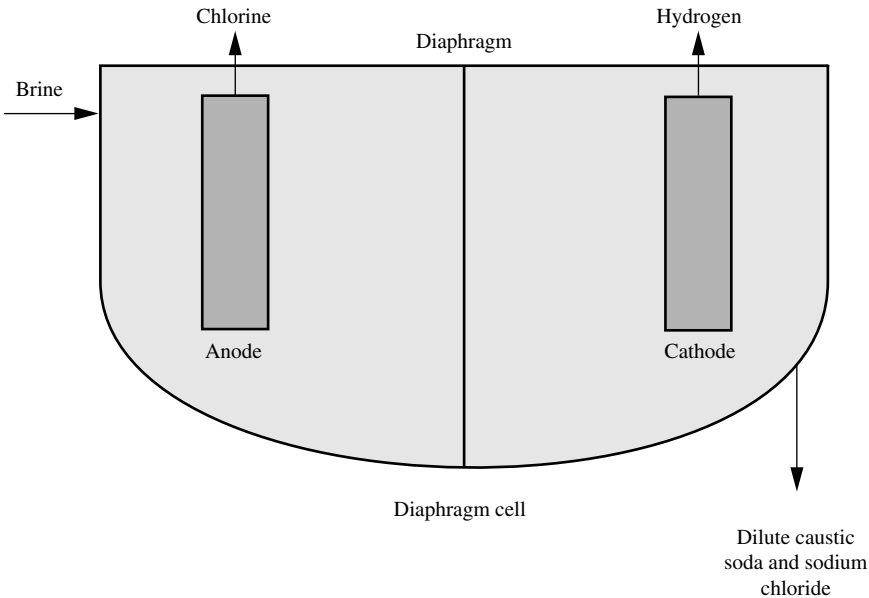


FIGURE 2 Schematic of the diaphragm cell.

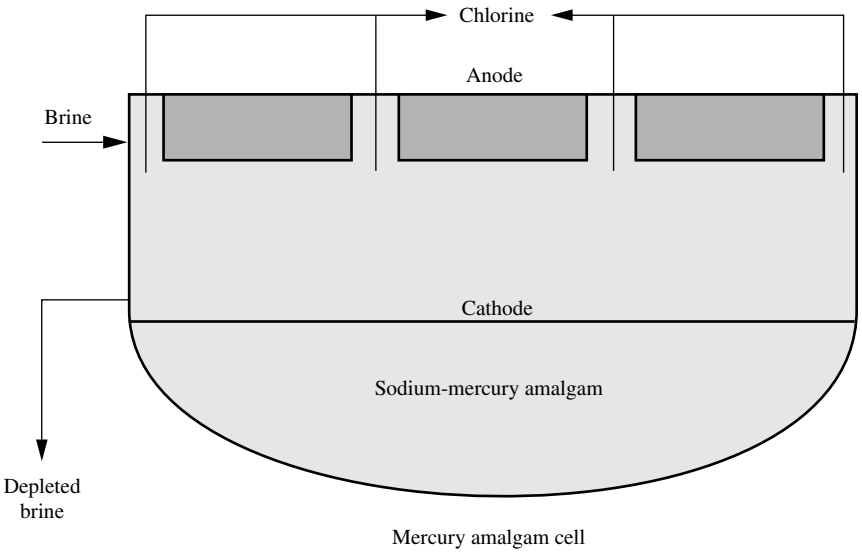


FIGURE 3 Schematic of the mercury cell.

amalgam enters a separate denuding chamber where the sodium metal reacts with water. Thus, the overall reaction is identical to that of the diaphragm cell.

Sodium hydroxide has diverse uses and is a reactant in organic and inorganic chemical manufacturing processes. It is also used in the petroleum, pulp and paper, textile, and alumina industries.

SODIUM HYPOCHLORITE

The most common method for manufacturing sodium hypochlorite is by the treatment of sodium hydroxide solution with gaseous chlorine.

$$2NaOH + Cl_2 \rightarrow 2NaOCl + NaCl + H_2O$$

Sodium hypochlorite is employed as a disinfectant and deodorant in dairies, creameries, water supplies, sewage disposal, and households. It is also used as bleach in laundries. As a bleaching agent, it is very useful for cotton, linen, jute, rayon, paper pulp, and oranges.

SODIUM METABISULFITE

See ***Sulfurous Acid.***

convert progesterone into 11 α-hydroxyprogesterone after which oxidation leads to the trione. Condensation with ethyl oxalate activates the appropriate carbon toward selective bromination to form the dibromide. Rearrangement followed by dehydrohalogenation is the next step, and the ketone at C-3 is protected as its ketal. Reaction with lithium aluminum hydride reduces the ester and the C-11 ketone to the alcohol. Acetylation of one of the alcohol groups (the less-hindered primary alcohol) and removal of the protecting group at C-3 then gives the unsaturated acetate, and osmium tetroxide and hydrogen peroxide oxidize the double bond to give hydrocortisone acetate, after which oxidation of the alcohol group and hydrolysis of the acetate gives cortisone.

STREPTOMYCIN

The commercial method for producing this compound involves aerobic submerged fermentation.

The structure of streptomycin indicates its highly hydrophilic nature, and it cannot be extracted by normal solvent procedures. Because of the strong-base characteristics of the two substituted guanidine groups, it may be treated as a cation and removed from the filtered solution by ion-exchange techniques.

STYRENE

Styrene (phenyl ethylene, vinyl benzene; freezing point: –30.6°C, boiling point: 145°C, density: 0.9059, flash point: 31.4°C) is made from ethylbenzene by dehydrogenation at high temperature (630°C) with various metal oxides as catalysts, including zinc, chromium, iron, or magnesium oxides coated on activated carbon, alumina, or bauxite (Fig. 1). Iron oxide on potassium carbonate is also used.

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

Most dehydrogenations do not occur readily even at high temperatures. The driving force for this reaction is the extension in conjugation that results, since the double bond on the side chain is in conjugation with the ring. Conditions must be controlled to avoid polymerization of the styrene and sulfur may be added to prevent polymerization. The crude product is a mixture of styrene, and ethylbenzene that is separated by vacuum distillation, after which the ethylbenzene is recycled. Usually a styrene plant is combined with an ethylbenzene plant when designed.

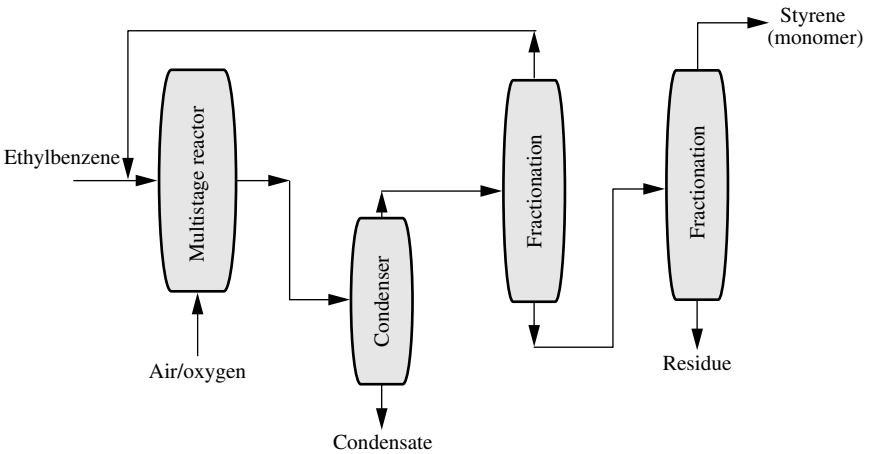


FIGURE 1 Manufacture of styrene from ethylbenzene.

An alternative method for the manufacture of styrene (the oxirane process), uses ethylbenzene that is oxidized to the hydroperoxide and reacts with propylene to give phenylmethylcarbinol (or methyl benzyl alcohol) and propylene oxide. The alcohol is then dehydrated at relatively low temperatures (180 to 400°C) by using an acidic silica gel (SiO_2) or titanium dioxide (TiO_2) catalyst.

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH(OOH)CH_3$$

$$C_6H_5CH(OOH)CH_3 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH(OH)CH_3 + CH_3CH_2\,CH_2O$$

$$C_6H_5CH(OH)CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2O$$

Other methods, such as the direct reaction of benzene and ethylene (Fig. 2) or from pyrolysis gasoline (Fig. 3) are also used to manufacture styrene.

The uses of styrene are dominated by polymer chemistry and involve polystyrene and its copolymers as used in various molded articles such as toys, bottles, and jars and foam for insulation and cushioning.

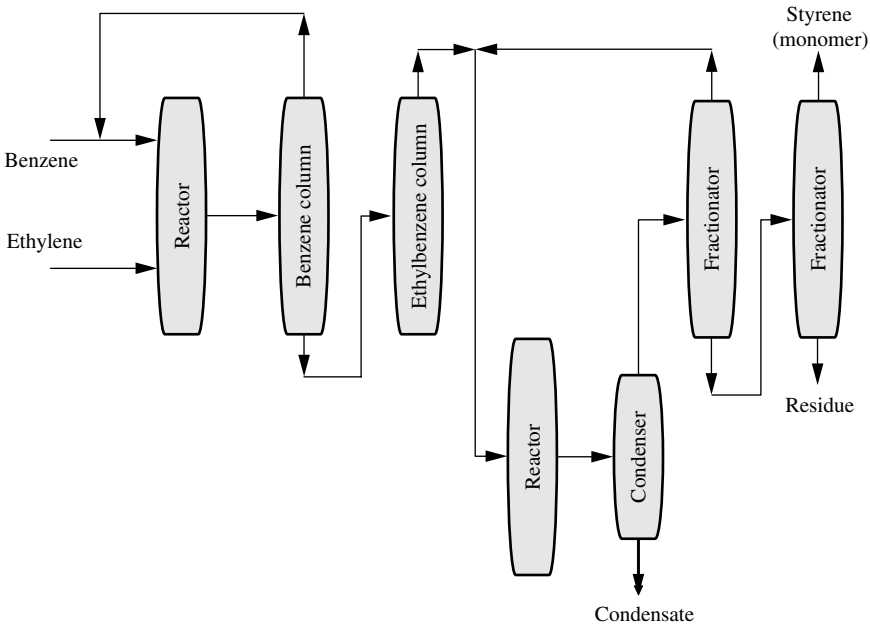


FIGURE 2 Manufacture of styrene from benzene and ethylene.

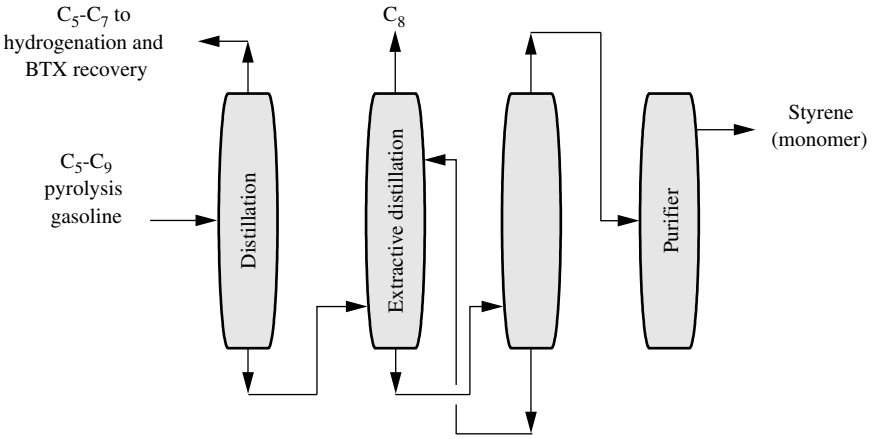


FIGURE 3 Manufacture of styrene from a gasoline fraction.

SULFONAMIDES

The physiologically active sulfonamide (sulfa) drugs involve variations of groups in place of the hydrogen of the sulfonamide moiety.

In the production of a sulfonamide compound, aniline is protected by acetylation to acetanilide to limit the chlorosulfonylation to the *para*-position. Acetylation deactivates the ring toward multielectrophilic attack. Various amines react with sulfonyl chloride to give acetylated sulfonamides. Hydrolysis then removes the acetyl group to give the active drug. Sometimes the drug is administered as its sodium salt, which is soluble in water.

Some common sulfa drugs have changes in the R, with sulfadiazine being probably the best for routine use. It is 8 times as active as sulfanilamide and exhibits fewer toxic reactions than most of the sulfonamides. Most of the common derivatives have an R group that is heterocyclic because of the greater absorption into the body but easier hydrolysis to the active sulfanilamide.

Sulfonamide compounds, although largely replaced by other, newer antibacterial compounds, are still used in treatment of certain infections.

SULFUR

Sulfur occurs naturally in the free state and in ores such as pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$).

Sulfur is recovered from natural sources such as calcite by the Frasch process (Fig. 1).

Sulfur is also a constituent of petroleum and natural gas (as H_2S). Thus, removing hydrogen sulfide from natural and refinery gases with absorbents such as monoethanolamine and/or diethanolamine also produces elemental sulfur. The hydrogen sulfide is then converted to elemental sulfur by the Claus or modified Claus process (Fig. 2).

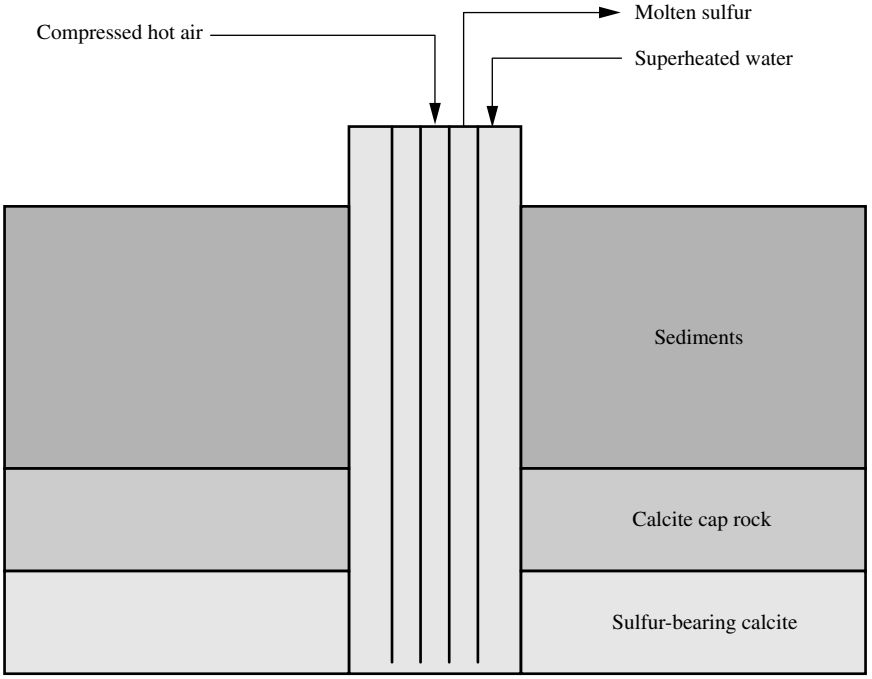


FIGURE 1 Sulfur production by the Frasch process.

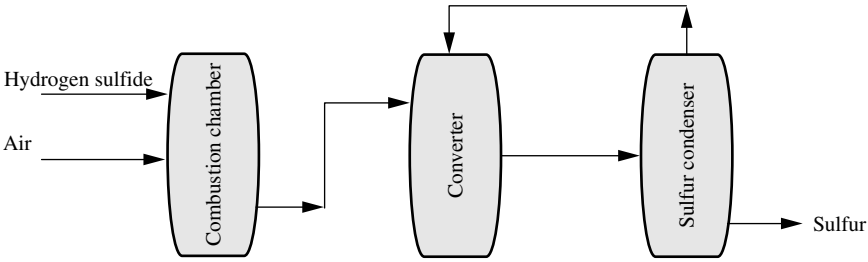


FIGURE 2 Sulfur production by the Claus process.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$
$$2SO_2 + 2H_2S \rightarrow 3S + H_2O$$

Although there are diverse uses for sulfur, the largest application is in the manufacture of sulfuric acid.

SULFUR DIOXIDE

Sulfur dioxide (boiling point, –10°C) is a gas that occurs as a result of the oxidation of sulfur as, for example, during combustion of sulfur-containing fuels.

Sulfur dioxide is manufactured as part of the contact process for making sulfuric acid. Sulfur and oxygen are burned at 1000°C (1830°F). With very careful control of the amount of air entering the combustion chamber, sulfur dioxide can be produced up to 18% by volume at a temperature of 1200°C. As the gases from the combustion chamber pass through the heat exchanger, they heat the water for the boilers. The cooled gases, containing from 16 to 18% sulfur dioxide, are pumped into the absorbers through acidproof pumps. The temperature of the vapors coming from the steaming tower depends upon its design, but usually runs about 70°C. The vapors are cooled and passed through a drying tower in which 98% sulfuric acid is used, although other drying agents may be employed. The sulfur dioxide is liquefied by compression and cooling.

Sulfur dioxide is used for refrigeration and also serves as raw material for the production of sulfuric acid. It is also used as a bleaching agent in the textile and food industries. It is an effective disinfectant and is employed as such for wooden kegs and barrels and brewery apparatus and for the prevention of mold in the drying of fruits. Sulfur dioxide efficiently controls fermentation in the making of wine. It is used in the sulfite process for paper pulp, as a liquid solvent in petroleum refining, and as a raw material in many plants in place of sulfites, bisulfites, or hydrosulfites.

See ***Sulfuric Acid.***

SULFURIC ACID

Sulfuric acid (oil of vitriol, H_2SO_4) is a colorless, oily liquid, dense, highly reactive, and miscible with water in all proportions. Heat is evolved when concentrated sulfuric acid is mixed with water and, as a safety precaution, the acid should be poured into the water rather than water poured into the acid. Anhydrous, 100% sulfuric acid, is a colorless, odorless, heavy, oily liquid (boiling point: 338°C with decomposition to 98.3% sulfuric acid and sulfur trioxide). Oleum is excess sulfur trioxide dissolved in sulfuric acid. For example, 20% oleum is a 20% sulfur trioxide–80% sulfuric acid mix. Sulfuric acid will dissolve most metals and the concentrated acid oxidizes, dehydrates, or sulfonates most organic compounds, sometimes causing charring.

The manufacture of sulfuric acid by the *lead chamber process* involves oxidation of sulfur to sulfur dioxide by oxygen, further oxidation of sulfur dioxide to sulfur trioxide with nitrogen dioxide, and, finally, hydrolysis of sulfur trioxide.

$$S + O_2 \rightarrow SO_2$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Modifications of the process include towers to recover excess nitrogen oxides and to increase the final acid concentration from 65% (*chamber acid*) to 78% (*tower acid*).

The *contact process* has evolved to become the method of choice for sulfuric acid manufacture because of the ability of the process to produce stronger acid.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the process (Fig. 1), sulfur and oxygen are converted to sulfur dioxide at 1000°C and then cooled to 420°C. The sulfur dioxide and oxygen enter the converter, which contains a catalyst such as vanadium pentoxide (V_2O_5). About 60 to 65% of the sulfur dioxide is converted by an exothermic reaction to sulfur trioxide in the first layer with a 2 to 4-second contact time. The gas leaves the converter at 600°C and is cooled to 400°C before it enters the second layer of catalyst. After the third layer, about 95% of the sulfur dioxide is converted into sulfur trioxide. The mixture is then fed to the initial absorption tower, where the sulfur trioxide is hydrated to sulfuric acid after which the gas mixture is reheated to 420°C and enters the fourth layer of catalyst that gives overall a 99.7% conversion of sulfur dioxide to sulfur trioxide. It is cooled and then fed to the final absorption tower and hydrated to sulfuric acid. The final sulfuric acid concentration is 98 to 99% (1 to 2% water). A small amount of this acid is recycled by adding some water and recirculating into the towers to pick up more sulfur trioxide.

Although sulfur is the common starting raw material, other sources of sulfur dioxide can be used, including iron, copper, lead, nickel, and zinc sulfides. Hydrogen sulfide, a by-product of petroleum refining and natural

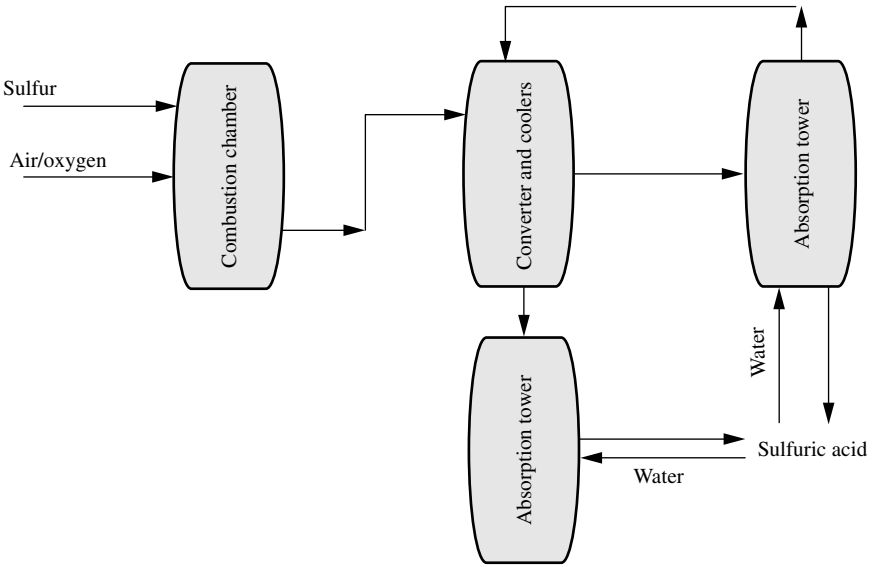


FIGURE 1 Manufacture of sulfuric acid by the contact process.

gas refining, can be burned to sulfur dioxide. Gypsum ($CaSO_4$) can also be used but needs high temperatures to be converted to sulfur dioxide. Other uses for sulfuric acid include the manufacture of fertilizers, chemicals, inorganic pigments, petroleum refining, etching, as a catalyst in alkylation processes, in electroplating baths, for pickling and other operations in iron and steel production, in rayon and film manufacture, in the making of explosives, and in nonferrous metallurgy

SULFUROUS ACID

Sulfurous acid (H_2SO_3) is a colorless liquid, prepared by dissolving sulfur dioxide (SO_2) in water. Reagent grade sulfurous acid contains approximately 6% sulfur dioxide in solution.

Sodium sulfite (Na_2SO_3) and sodium bisulfite (sodium hydrogen sulfite, $NaHSO_3$) are formed by the reaction of sulfurous acid and sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) in the proper proportions and concentrations. When dry, on heating sodium sulfite yields sodium sulfate (Na_2SO_4) and sodium sulfide (Na_2S).

Crystalline sulfites are obtained by warming the corresponding bisulfite solutions. Calcium hydrogen sulfite [$Ca(HSO_3)_2$] is used in conjunction with excess sulfurous acid in converting wood to paper pulp. Sodium sulfite and silver nitrate solutions react to yield silver sulfite (Ag_2SO_3), a white precipitate, which upon boiling decomposes, forming silver sulfide, a brown precipitate.

Sulfurous acid forms dimethyl sulfite ($(CH_3O)_2SO$, boiling point: 126°C) with methyl alcohol and diethyl sulfite [$(C_2H_5O)_2SO$, boiling point: 161°C] with ethyl alcohol. As a bleaching agent, sulfurous acid is used for whitening wool, silk, feathers, sponge, straw, wood, and other natural products. In some areas, its use is permitted for bleaching and preserving dried fruits.

SULFUR TRIOXIDE

Sulfur trioxide is a pungent gas that is produced by the oxidation of sulfur dioxide or the complete combustion of sulfur with oxygen. It is also manufactured by distillation of strong oleum ($H_2SO_4 \cdot SO_3$).

Liquid sulfur trioxide is used for sulfonation, especially in the manufacture of detergents. In the past, the difficulty was the instability of the sulfur trioxide. However, under the trade name Sulfans®, stabilized forms of sulfur trioxide are available; several patented inhibitors such as boron compounds, methane sulfonyl chloride, sulfur, tellurium, and phosphorus oxychloride inhibit crystallization or conversion to a polymer.

See ***Sulfuric Acid.***

SUPERPHOSPHATES

The acidification of phosphate rock to produce superphosphate is an important method of making phosphate available for fertilizer purposes.

$$CaH_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2CaSO_4 \cdot 2H_2O$$

$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

The manufacture of superphosphate involves:

1. Preparation of phosphate rock
2. Mixing with acid
3. Curing and drying of the original slurry by completion of the reactions
4. Excavation, milling, and bagging of the finished product.

These steps can be performed in stepwise processes or continuous processes.

See ***Phosphoric Acid, Sodium Phosphate.***

SURFACTANTS

Surfactants are chemicals that, when dissolved in water or another solvent, orient themselves at the interface between the liquid and a second solid, liquid, or gaseous phase and modify the properties of the interface.

Surfactants, as a chemical class, have a common molecular similarity insofar as part of the molecule has a long nonpolar (frequently hydrocarbon, hydrophobic) chain that promotes oil solubility and water insolubility and a polar (hydrophilic) part. The hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain. The hydrophilic functional group may vary widely and may be anionic, e.g., SO_3^{2-}, cationic, e.g., $-N(CH_3)_3+$ or C_5H_5N+; or nonionic, e.g., $-(OCH_2CH_2)-OH$.

In the anionic class, the most used compounds are linear alkylbenzene sulfonates from petroleum and alkyl sulfates from animal and vegetable fats. The straight-chain paraffins or olefins needed are produced from petroleum.

Linear olefins are prepared by dehydrogenation of paraffins, by polymerization of ethylene to *a*-olefins using a triethyl aluminum catalyst (Ziegler-type catalyst), by cracking paraffin wax, or by dehydrohalogenation of alkyl halides.

a-olefins or alkane halides can be used to alkylate benzene through the Friedel-Crafts reaction, employing hydrofluoric acid or aluminum fluoride as a catalyst.

The Ziegler catalytic procedure for converting *a*-olefins to fatty alcohols and the methyl ester hydrogenation process are the important methods for preparing fatty alcohols.

Surfactants can be divided into four general areas: cationic surfactants, anionic surfactants, nonionic surfactants, and amphoteric surfactants. Major anionic surfactants are soaps, linear alcohol sulfates, linear alcohol ethoxysulfates, and linear alkylbenzenesulfonates.

See ***Surfactants (Amphoteric), Surfactants (Anionic), Surfactants (Cationic), Surfactants (Nonionic).***

SURFACTANTS (AMPHOTERIC)

Amphoteric surfactants carry both a positive and a negative charge in the organic part of the molecule. They still have a long hydrocarbon chain as the hydrophobic tail and behave as anionic surfactants or cationic surfactants, depending on the pH.

Amphoteric surfactants are used in shampoos and can be used with alkalis for greasy surfaces as well as in acids for rusty surfaces.

See ***Surfactants***, ***Surfactants (Anionic)***, ***Surfactants (Cationic)***, ***Surfactants (Nonionic)***.

SURFACTANTS (ANIONIC)

Anionic surfactants have a molecular structure in which the long hydrophobic alkyl chain is in the anionic part of the molecule.

α-olefin sulfonates are manufactured by the reaction of C_{12}–C_{18} α-olefins with sulfur trioxide followed by reaction with caustic soda. The product is a complex mixture of compounds, and disulfonates are also formed.

Secondary alkanesulfonates are manufactured by the action of sulfur dioxide and air directly on C_{14}–C_{18} *n*-paraffins (a sulfoxidation reaction), and the sulfonate group can appear in most positions on the chain.

The linear alcohols can be made from other long-chain linear materials, but a process that involves use of a triethylaluminum catalyst allows their formation directly from ethylene and oxygen.

$$n CH_2{=}CH_2 + O_2\ (+ Et_3Al) \rightarrow R{-}CH_2{-}OH\ (+ Et_3Al)$$

Alcohol ethoxysulfates are made by reaction of 3 to 7 mol of ethylene oxide with a linear C_{12}–C_{14} primary alcohol to give a low-molecular-weight ethoxylate.

Alkyl groups for linear alkylbenzenesulfonate detergents are made through linear α-olefins. *n*-alkanes can be dehydrogenated to α-olefins, which then can undergo a Friedel-Crafts reaction with benzene as described above for the nonlinear olefins. Sulfonation and basification gives the linear alkylbenzenesulfonate detergent.

Alternatively, linear α-olefins can be made from ethylene by using Ziegler catalysts to give the ethylene oligomer with a double-bonded end group.

$$6CH_2{=}CH_2 \rightarrow C_{10}H_{21}CH{=}CH_2$$

Linear alkylbenzenesulfonate detergents made from the chlorination route have lower amounts of 2-phenyl product. Use of the α-olefins gives greater 2-phenyl content, which in turn changes the surfactant action somewhat.

See ***Surfactants***, ***Surfactants (Amphoteric)***, ***Surfactants (Cationic)***, ***Surfactants (Nonionic)***.

SURFACTANTS (CATIONIC)

Cationic surfactants are generally nitrogen compounds and many are quaternary nitrogen compounds, such as tallow fatty acid trimethylammonium chloride. In the more general structure $R^1R^2R^3R^4N^+X^-$, R^1 is a long alkyl chain, the other R moieties may be alkyl or hydrogen, and X^- is halogen or sulfate ion.

The long hydrocarbon chain is derived from naturally occurring fats or triglycerides, that is, triesters of glycerol having long chain acids with an even number of carbons, being of animal or vegetable origin. A common source for cationic surfactants is inedible tallow from meat packing plants. If the fatty acid is required, the ester is hydrolyzed at high temperature and pressure, or with a catalyst such as zinc oxide or sulfuric and sulfonic acid mixtures. The fatty acid is then converted into the quaternary nitrogen salt.

Cationic surfactants have applications such as inhibiting the growth of bacteria, inhibiting corrosion, separating phosphate ore from silica and potassium chloride from sodium chloride (flotation agents), and they serve well as fabric softeners, antistatic agents, and hair conditioners.

See ***Surfactants***, ***Surfactants (Amphoteric)***, ***Surfactants (Anionic)***, ***Surfactants (Nonionic)***.

SURFACTANTS (NONIONIC)

Nonionic surfactants have a molecular arrangement in which there is a nonpolar hydrophobic portion and a more polar, but not ionic, hydrophilic part capable of hydrogen bonding with water.

The major nonionic surfactants have been the reaction products of ethylene oxide and nonylphenol. Dehydrogenation of *n*-alkanes from petroleum (C_9H_{20}) is the source of the linear nonene.

They are now being replaced by the polyoxyethylene derivative of straight-chain primary or secondary alcohols with C_{10}–C_{18}. These linear alcohol ethoxylate nonionic surfactants are more biodegradable than nonylphenol derivatives and have better detergent properties than linear alkylbenzenesulfonate.

$$C_{14}H_{29}\text{–OH} + n\text{CH}_2\text{CH}_2\text{–O} \rightarrow C_{14}H_{29}\text{–O(CH}_2\text{CH}_2\text{O)}_n\text{H}$$

See ***Surfactants***, ***Surfactants (Amphoteric)***, ***Surfactants (Anionic)***, ***Surfactants (Cationic).***

SYNTHESIS GAS

Synthesis gas (syngas) is a mixture of carbon monoxide and hydrogen that is produced from the reaction of carbon (usually coal or coke or similar carbonaceous material) with steam.

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$C + CO_2 \rightarrow 2CO$$

There are three reactor types for gasification processes: (1) a gasifier reactor, (2) a devolatilizer, and (3) a hydrogasifier with the choice of a particular design, e.g., whether or not two stages should be involved, depending on the ultimate product gas desired. Reactors may also be designed to operate over a range of pressure from atmospheric to high pressure and gasification processes can also be segregated according to the bed types: (1) fixed bed, (2) moving bed, (3) fluidized bed, and (4) entrained bed.

Purification of synthesis gas is an important aspect of the process and involves the removal of carbon oxides to prevent poisoning of the catalyst. An absorption process (ethanolamine or hot carbonate) is used to remove the bulk of the carbon dioxide, followed by methanation of the residual carbon oxides in the methanator.

In the production of paraffins, the mixture of carbon monoxide and hydrogen is enriched with hydrogen from the water-gas catalytic (Bosch) process, i.e., shift reaction (Fig. 1), and passed over a cobalt-thoria catalyst to form straight chain (linear) paraffins, olefins, and alcohols (Fischer-Tropsch synthesis):

$$n\text{CO} + (2n + 1)\text{H}_2\ (+ \text{ cobalt catalyst}) \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$$

$$2n\text{CO} + (n + 1)\text{H}_2\ (+ \text{ iron catalyst}) \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{CO}_2$$

$$n\text{CO} + 2n\text{H}_2\ (+ \text{ cobalt catalyst}) \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$$

$$2n\text{CO} + n\text{H}_2\ (+ \text{ iron catalyst}) \rightarrow \text{C}_n\text{H}_{2n} + n\text{CO}_2$$

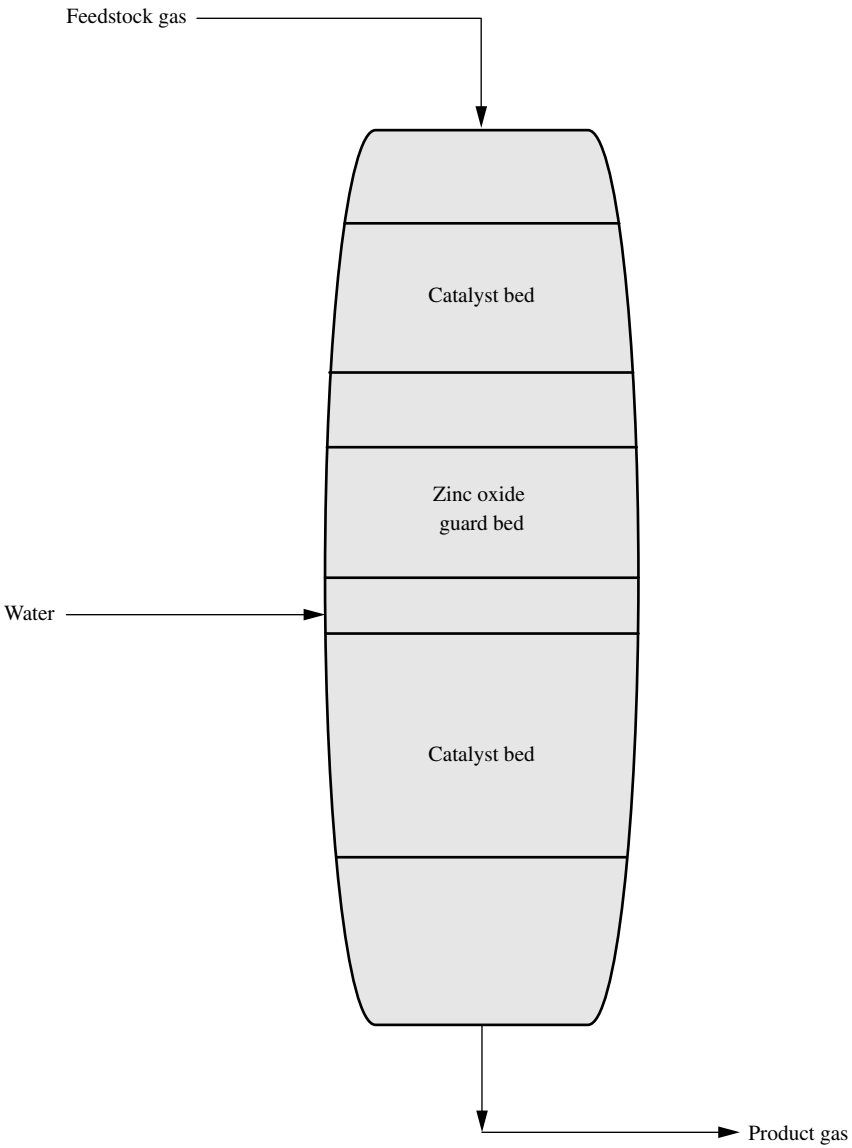


FIGURE 1 Schematic of a shift converter.

$$n\mathrm{CO} + 2n\mathrm{H_2}\ (+\ \text{cobalt catalyst}) \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H_2O}$$

$$(2n-1)\mathrm{CO} + (n+1)\mathrm{H_2}\ (+\ \text{iron catalyst}) \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{CO_2}$$

Synthesis gas is widely used as a starting material for a variety of chemicals (Fig. 2).

Starting material	Reaction type	Product
Synthesis gas (carbon monoxide + hydrogen)	Oxo reaction	Oxo products
	Shift reaction	Hydrogen
	Shift reaction	Methyl alcohol
	Shift reaction	Ammonia
	Shift reaction and methanation	Substitute natural gas
	Organic synthesis	Hydroquinone
	Homologation	Ethyl alcohol
	Carbonylation	Acetic acid
	Fischer-Tropsch	Ethylene
	Fischer-Tropsch	Paraffins
	Glycol synthesis	Ethylene glycol

FIGURE 2 Chemicals from synthesis gas.